

A Polychlorinated Dibenzofuran and Related
Compounds in an Estuarine Ecosystem

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A Polychlorinated Dibenzofuran and Related Compounds in an Estuarine Ecosystem

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■ A 2,4,8-trichlorodibenzofuran, a tetrachlorodiphenyl ether, and a trichlorodiphenyl ether have been identified in samples of edible marine organisms and suspended particulate material obtained from Narragansett Bay, RI. Rapid declines in the concentrations of these compounds with increased distance from the highly polluted northern bay strongly suggest an upper-bay source. Comparisons of the characteristics of this contamination with those from known chemical-plant inputs and with those in PCBs, chlorophenols, and wastes from municipal incinerators indicate chemical-plant discharges as the most likely source.

Introduction

The use of Narragansett Bay, RI, both as a disposal site for industrial and municipal wastes and as a commercial fishery makes it an excellent location for studies on the accumulation of toxic organic compounds in estuarine organisms. The objective of the present study was to identify the organic compounds accumulated by transplanted mussels and by indigenous bay organisms. In the course of this study 2,4,8-trichlorodibenzofuran (tri-CDF), a possible precursor tetrachlorodiphenyl ether (tetra-CDE), and a trichlorodiphenyl ether (tri-CDE) were identified in extracts of organisms and in samples of suspended particulate material. The presence of

the tri-CDF was of special interest because of the high toxicity generally associated with chlorinated dibenzofurans (1). These compounds have been found as contaminants in PCBs (2-6) and in fly ash from municipal incinerators (7), and PCDFs and precursors have been identified in chlorophenols and related compounds (8-11). While some potential sources have been identified and the environmental significance of reactions forming PCDFs from precursor compounds has been emphasized (9, 12-14), until recently PCDFs have not been found in environmental samples (15, 16). It was suggested that finding PCDFs in the environment from a PCB source was not likely because of the low level of PCDFs in PCBs and because of sensitivity limitations of analytical instrumentation (17). However, a more sensitive technique, negative chemical ionization mass spectrometry, recently has identified PCDFs (most likely of a PCB origin) in environmental samples from some rivers and lakes of the United States (18).

Of particular interest to the present study was the detection of tri- and tetra-CDEs in the wastewater (19) of a chemical manufacturing plant located on the Pawtuxet River (a tributary of the Providence River (Figure 1)) and the finding of a tri-CDF (structural isomer not identified) in the plant's wastewater (19-21), the Pawtuxet River (19), and Narragansett Bay (19).

Methods

Mussels (*Mytilus edulis*) used in this study were part of a program utilizing these organisms as biomonitors of pollution in estuarine systems (22). The mussels were held in cages for 2 months in 1978 or 4 months in 1979 at stations on a transect from the highly polluted northern end of the bay to the less polluted southern end (Figure 1). The other organism samples were obtained by divers from the mid and lower bay in the summer of 1979. Suspended particulates were collected at transect stations in the summer of 1979 by drawing bay water through glass-fiber filters which had been heated in a muffle furnace before use (550 °C for 6 h).

Following sample collection, filters were oven dried to constant weight (32 °C) and extracted by recycling CH_2Cl_2 through them for 2 h with a Teflon pump.

Organism samples were extracted by polytron homogenization with acetone and then Freon 113. Acetone extracts were partitioned between water and Freon, and the Freon extracts were combined and passed through a 2 × 25 cm column of activated silica gel. Following volume reduction and solvent exchange to hexane, extracts were separated into fractions by column chromatography (0.9 × 45 cm) on deactivated (5% w/w H_2O) silica gel. The PCB fraction, which contained the compounds of interest, was eluted in 50 mL of *n*-pentane. Capillary column electron capture gas chromatography was performed on a 60-m SE-54 column in a Hewlett-Packard 5840-A gas chromatograph. Mass spectra were obtained with the same column installed in a Shimadzu Model 4CM gas chromatograph directly coupled to a Finnegan 1015 mass spectrometer with a RDS data system. The concentrations of tri-CDF were determined on the basis of the response of a 2,4,8-trichlorodibenzofuran standard. The concentrations of both polychlorinated diphenyl ethers (PCDEs) were calculated by comparison with the response of 2',3,4,4'-tetra-CDE. Since the results (Table I) were not corrected for procedural losses, they probably represent conservative estimates of the actual concentrations. Reagent blanks processed along with these samples showed no peaks throughout the PCB region, while samples collected from an area outside of Narragansett Bay showed PCBs, but not the tri-CDF or the tri- or tetra-CDEs.

Since reactions converting precursor compounds into chlorinated dioxin compounds in heated gas-chromatographic

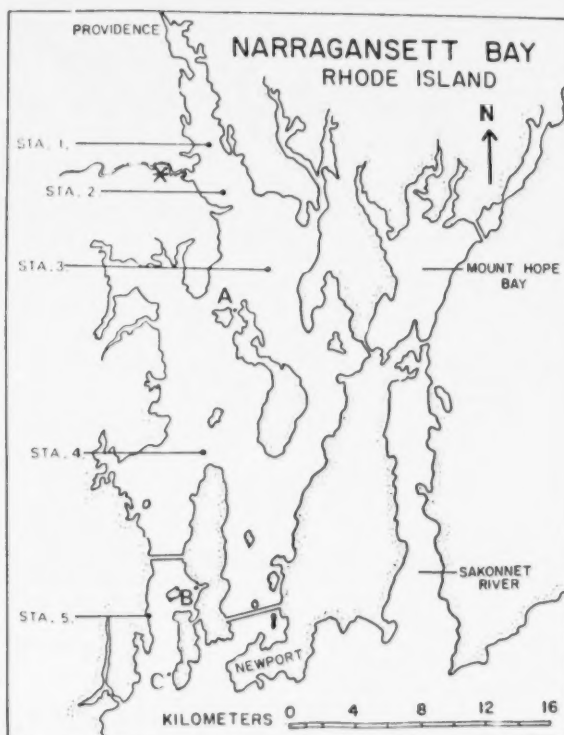


Figure 1. Map of Narragansett Bay showing station locations. Numbers refer to caged mussel stations on a transect from the highly polluted upper bay to the less polluted lower bay. A, B, and C refer to collection stations for clams, lobster, and lower-bay suspended particulate material, respectively. (*) Location of Pawtuxet River.

injection ports have been reported (23), an experiment was conducted to compare analyses using on-column injection (which avoids a heated injection port (24)) with those using a conventional heated injection port. The results showed that sample components were not interconverted during GC analysis. Other experiments, including a GC-MS analysis of a mussel extract which had not been subjected to column chromatography and another which carried a column chromatographic fraction (containing tri-CDF and PCDEs) back through the entire analytical procedure a second time, provided additional evidence that interconversion reactions were not occurring as a result of the analytical procedures utilized.

Results and Discussion

A representative electron capture detection gas chromatogram obtained from extracts of mussels caged in the highly polluted upper bay from April to August, 1979, is shown in Figure 2. This general pattern of peaks is observed in other 1979 Narragansett Bay samples, including mussels which had been caged at other transect stations (Figure 1), suspended particulate material from the upper and lower bay, clams (*Mercenaria mercenaria*) from the midbay, and the hepatopancreas of a lobster (*Homarus americanus*) from the lower bay. Similar patterns also are found in mussels caged at stations in the bay in 1978. One of the major peaks in electron capture gas chromatograms from the samples analyzed is a chlorinated dibenzofuran. A mass spectrum of this compound from a mussel obtained at a highly polluted north-bay station is compared with the spectrum of a 2,4,8-tri-CDF standard in Figure 3. The excellent agreement of these spectra and comparisons of the spectrum in Figure 3A with those reported for PCDFs in the literature (2, 8, 12, 25) confirm the tri-CDF

Table I. Concentrations ^a of Compounds in Narragansett Bay Samples

location (km from Providence)	station	sample type ^b	exposure yr	caged (mussels only) months	tri-CDE	tetra-CDE	tri-CDF
upper bay (3)	1	Mus(MS)	1979	April-Aug	46	198	730
		Mus(MS)	1978	June-Aug	61	228	643
		SP*(MS)	1979		0.03 ppt	0.06 ppt	0.25 ppt
upper bay (7)	2	Mus(MS)	1979	April-Aug	105	391	1100
		duplicate	1979	April-Aug	125	416	1180
midbay (13)	3	Mus	1979	April-Aug	89	296	482
midbay (15)	A	C	1979		2.4	9.1	26
lower bay (23)	4	Mus	1979	April-Aug	5.3	32	67
		Mus	1978	June-Aug	4.5	32	53
lower bay (34)	5	Mus	1979	April-Aug	3.6	24	52
		LHP(MS)	1979		82	144	1260
lower bay (37)	C	SP*	1979		X ^c	X ^c	X ^c

^a In ppb (dry) except where noted. ^b Mus = mussel (*Mytilus edulis*) from cages. C = clam (*Mercenaria mercenaria*); conversion to dry wt from mussel dry wt data. LHP = lobster hepatopancreas. SP = suspended particulates; numbers are estimated in parts per trillion from the volume of water filtered. (*) These analyses require manipulation of very small volumes of solvent and therefore are subject to considerable uncertainty. (MS) = Peak identities checked with mass spectrum. Other identifications by retention time. Concentrations are corrected for procedural losses. ^c A recognizable gas chromatogram was obtained, and the concentrations on suspended particulate material were estimated to be ~20X lower than in the upper bay. More accurate quantification was not possible at these levels.

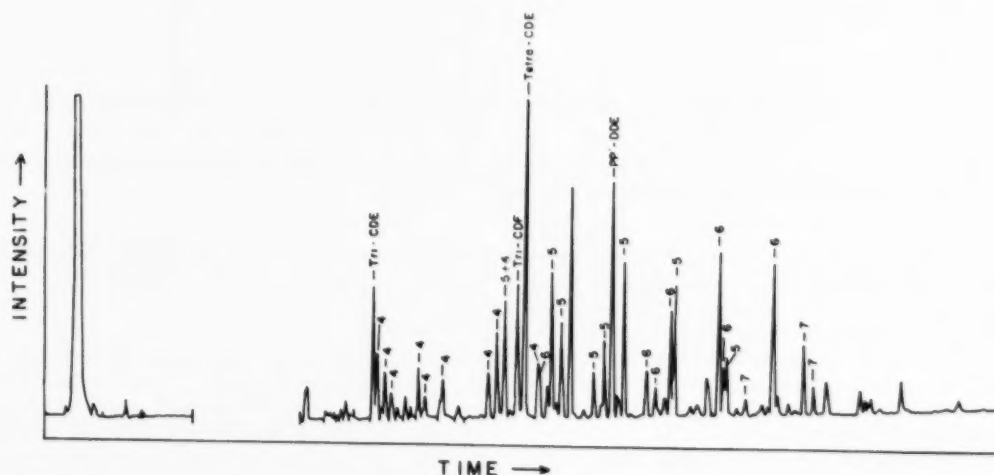


Figure 2. A representative electron capture detection gas chromatogram obtained from a column chromatographic fraction from upper-bay (highly polluted) mussels (*Mytilus edulis*). This chromatogram was obtained on a 60-m SE-54 column operated with He carrier gas at 24 cm/s; 80 °C for 4 min, 80–120 °C at 5 °C/min, 120–270 °C at 1 °C/min, 270 °C for 15 min. Similar chromatograms were obtained by summing extracted ion current profiles for the molecular ions of the PCBs, the pesticides, the chlorinated dibenzofurans, and the chlorinated diphenyl ethers when this column was directly coupled to a Finnegan quadrupole 1015 GC-MS (EI (70 eV)) interfaced to a RDS data system. Full mass range spectra were obtained for identifications. Numbers above the peaks refer to the number of chlorine atoms on the PCBs.

identification. The tri-CDF in environmental samples was identified as the 2,4,8-trichloro isomer on the basis of comparison of retention times on glass capillary columns and by coinjection of the 2,4,8-trichlorodibenzofuran standard with sample extracts. Another peak eluting just after the tri-CDF is identified as a tetra-CDE. An alternative structure considered for this compound is the tetrachlorobiphenylol, which may have been introduced directly to the bay or may have resulted from the action of biological systems on PCBs (13). This biphenylol structural possibility is eliminated, however, because of the insolubility of this compound in base (13), its elution behavior during column chromatography on silica gel and on alumina (5), and the excellent match of its mass spectrum with that of a tetra-CDE standard. In a similar manner a peak eluting in an earlier portion of the chromatograms is identified as a tri-CDE.

Supplemental GC-MS analyses at another EPA laboratory also identified the tri-CDF and the tri- and tetra-CDEs in an extract from an upper-bay mussel (26).

The rapid decrease in concentrations of tri-CDF and tri- and tetra-CDEs with increased distance from Providence (Table 1) indicates an upper-bay source for these compounds.

One potential source for these compounds is a chemical plant which discharges wastes into the Pawtuxet River—a tributary of the Providence River (Figure 1). The tri-CDF (found in wastewater (19–21) and in the sediment and waters of the bay (19)) and the tri- and tetra-CDEs (detected only in wastewater from the plant (19)) were believed to be by-products from the manufacture of 2,4,4'-trichloro-2'-hydroxydiphenyl ether. Since there are numerous other industrial and municipal inputs to the bay, other potential sources for these compounds were considered.

PCDFs have been found in municipal fly ash (6) and as contaminants in PCBs (2, 5, 16) and chlorophenols (8–10). Each of these sources, however, showed several positional isomers for several PCDF homologues, while only a single isomer was found in the present study.

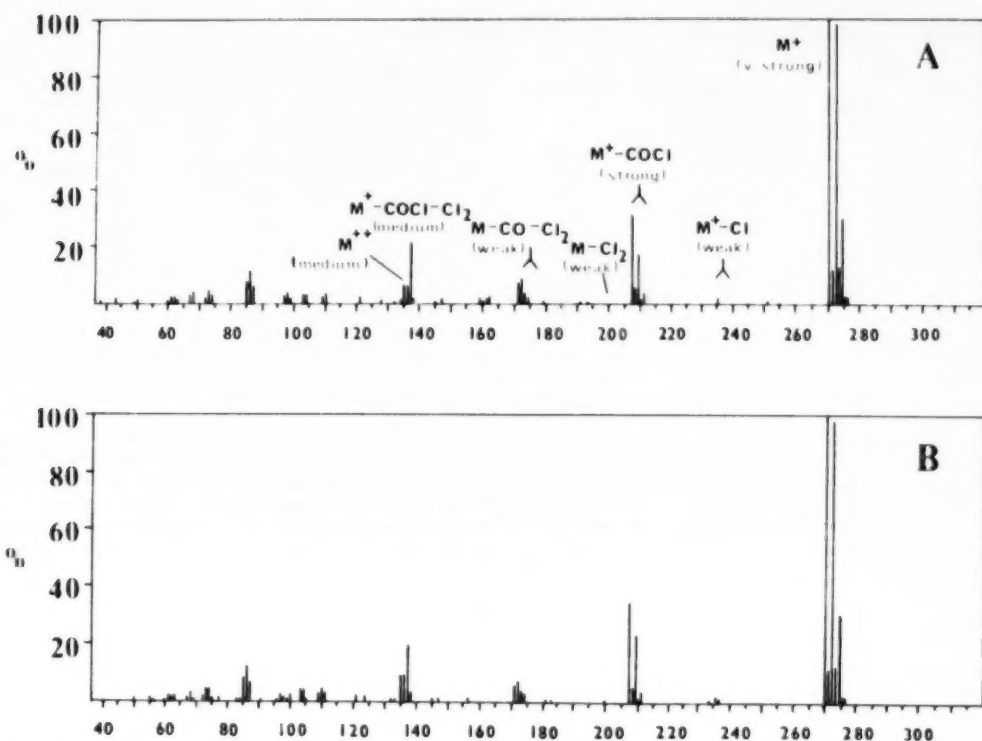


Figure 3. (A) Mass spectrum from peak identified as tri-CDF in Figure 1. Fragment ions and statements of intensity are as predicted for chlorinated dibenzofurans from ref 7. (B) Mass spectrum of a 2,4,8-trichlorodibenzofuran standard.

An analysis of 13 fish, a sediment, and a turtle from several rivers and lakes from the United States by the highly sensitive technique of chemical ionization mass spectrometry found PCDF homologues in 5 fish, the sediment, and the turtle (18). In general, several PCDF homologues were present, and, since the penta-CDF isomers dominated, as found in a majority of PCB mixtures analyzed (6), the authors suggested PCBs as a source for these PCDF contaminants.

The environmental significance of reactions forming PCDFs from precursor compounds has been emphasized (8, 12-14). Of particular interest to the present study is the photochemical conversion of a tetra-CDE to a tri-CDF (14). While this reaction may be operative in Narragansett Bay and thereby constitute another formation pathway for the tri-CDF, present data are insufficient to document its occurrence.

In 1968 hundreds of Japanese people developed Yusho disease from eating rice oil contaminated by PCBs containing an abnormally high level of PCDFs (6). While the cause of this disease was reported as PCB poisoning (27), some involvement of the PCDFs was suggested (6). It is emphasized that the levels of PCDF consumed by Yusho patients (~20 mg) (6) were enormous compared with those found here and that the PCDF contamination in the Yusho oil contained ~40 isomers, while only one was identified in this study.

The present study identified CDEs and 2,4,8-trichlorodibenzofuran in edible marine organisms and suspended particulate material from Narragansett Bay, RI. The concentrations of these compounds were found to decrease with increased distance from the proposed source area (upper bay), but these compounds were also detected in samples from less polluted (lower bay) sampling sites. Of the potential sources considered for these compounds, the most likely was the discharge of wastes from the chemical industry.

The extent of PCDF and PCDE contamination in other estuaries is unknown. The high toxicity generally associated with PCDFs calls for further documentation of their distri-

butions throughout the coastal United States and for rapid identification and abatement of their sources.

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